

NASA TECHNICAL
MEMORANDUM

NASA TM X-64086

(NASA-TM-X-64086) TEST OF LOX
COMPATIBILITY FOR ASPHALT AND CONCRETE
RUNWAY MATERIALS (NASA) ~~34~~ p HC \$3.75

37

CSCL 01E

N74-11091

Unclass

G3/11 21994

NASA TM X-64086



TEST OF LOX COMPATIBILITY FOR ASPHALT
AND CONCRETE RUNWAY MATERIALS

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December 1973

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STANDARD TITLE PAGE

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|--|--|--|--|--|--------------------------|
| 1. Report No. NASA TM X-64086 | | 2. Government Accession No. | | 3. Recipient's Catalog No. | |
| 4. Title and Subtitle Test of LOX Compatibility for Asphalt and Concrete Runway Materials | | | | 5. Report Date December 1973 | |
| | | | | 6. Performing Organization Code S0-LAB-4 | |
| 7. Author(s) C.V. Moyers, C.J. Bryan, and B.J. Lockhart | | | | 8. Performing Organization Report No. MTB 238-72 | |
| 9. Performing Organization Name and Address Materials Testing Branch Analytical Laboratories Division Kennedy Space Center, Florida | | | | 10. Work Unit No. | |
| | | | | 11. Contract or Grant No. | |
| 12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546 | | | | 13. Type of Report and Period Covered Technical Memorandum | |
| | | | | 14. Sponsoring Agency Code | |
| 15. Supplementary Notes | | | | | |
| 16. Abstract <p>A literature survey and a telephone canvass of producers and users of LOX yielded one report of an accident resulting from a LOX spill on asphalt, one discussion of hazardous conditions, and an unreferenced mention of an incident.</p> <p>Laboratory tests using standard LOX impact apparatus yielded reactions with both old and new asphalt, but none with concrete. In the final test, using a larger sample of asphalt, the reaction caused extensive damage to equipment.</p> <p>Initial field experiments using 2-meter square asphalt slabs covered with LOX, conducted during rainy weather, achieved no reaction with plummets, and limited reaction with a blasting cap as a reaction initiator. In a final plummet-initiated test on a dry slab, a violent reaction, which appeared to have propagated over the entire slab surface, destroyed the plummet fixture and threw fragments as far as 48 meters.</p> | | | | | |
| 17. Key Words Paving Materials Liquid Oxygen Compatibility | | | 18. Distribution Statement Unlimited | | |
| 19. Security Classif.(of this report) Unclassified | | 20. Security Classif.(of this page) Unclassified | | 21. No. of Pages 33 37 | 22. Price 3.75 |

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TEST OF LOX COMPATIBILITY FOR ASPHALT AND CONCRETE RUNWAY MATERIALS

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INTRODUCTION

On November 15, 1972, the Materials Testing Branch was requested to investigate reactions between asphalt and concrete pavement and LOX (LO_2). The investigation was conducted in three parts:

1. A literature survey was performed to learn what is available in published reports of experiments and accidents. In addition, producers and users of LO_2 were canvassed by telephone for possible unreported incidents.
2. Laboratory tests were conducted, using a standard LO_2 impact test apparatus.
3. Field experiments were performed, using 2-meter square slabs of asphalt pavement covered with LO_2 . Plummets and an explosive device were used as reaction initiators.

A brief summary to this study has been published in the May 1973 issue of the Fire Journal (Reference 1).

EVALUATION PROCEDURE AND RESULTS

Literature Survey

Apparently very few documented reports of accidents resulting from LO_2 spills on asphalt are available. In this survey, it was possible to obtain only one such report,

an explosion in Rocketdyne's LOX storage area (Reference 2). Another article, describing a general condition which may produce a hazardous environment, is reported in a Cryogenic Safety Conference Proceedings (Reference 3). A third incident was mentioned without reference to its source in a Safety Feature appearing in Industrial and Engineering Chemistry (Reference 4). Also, see Appendix A.

The National Fire Protection Association Standard for Bulk Oxygen Systems at Consumer Sites, NFPA No. 50-1971, included the following: "Where oxygen is stored as a liquid, noncombustible surfacing shall be provided in an area extending at least 3 feet from points at ground level upon which any leakage of liquid oxygen might fall during operation of the system and filling of a storage container. Such an area under liquid delivery connections of mobile supply equipment shall be at least the full width of the vehicle and at least 8 feet in the transverse direction.

NOTE 1: For purposes of this Standard, asphaltic or bitumastic paving is considered to be combustible.

NOTE 2: The slope, if any, of such areas shall consider possible flow of spilled liquid oxygen to adjacent combustible material."

Several individuals with the oxygen or associated industries were contacted by telephone concerning reports of accidents involving LO₂ and asphalt. The following are summaries of these contacts.

1. L. G. Matthews, Union Carbide Corporation, Linde Division, Tarrytown, N. Y., has heard of several reactions, but knows of only verbal reports. He recalled a possible incident involving North American on the West Coast several years ago, but again he could not verify this.

2. W. L. Walls, NFPA, Boston, Mass., recalled only hearing about a couple of incidents. He remembered hearing of one involving a fire truck driving over pavement on which LO₂ had been spilled, blowing a tire and fracturing a wheel; but, again could not verify with a report or location.

3. R. Watson, Bureau of Mines, Pittsburgh, Pa., had not heard of any accidents, but suggested that Air Products be contacted in reference to a safety conference they sponsored in 1959.

4. W. L. Ball, Air Products and Chemical, Inc., Allentown, Pa., provided information on the accident at Rocketdyne and the location of the Cryogenic Safety reference.

5. J. J. Crowe, Air Reduction, Union, N. J., knew personally of no such incidents.

6. L. H. Flanders, Factory Mutual Research Corporation, Boston, Mass., provided the reference in Industrial and Engineering Chemistry.

Laboratory Tests

Several LO_2 impact compatibility tests were performed on asphalt and concrete paving materials, by the procedure defined in MSFC SPEC-106-B. The first series of tests evaluated both new and old asphalts in two different thicknesses (approximately 0.19 cm and 0.64 cm) at 10 kg-m. A high percentage of reactions was observed on both the new and old materials; however, the more violent reactions occurred in the thicker samples of old asphalt.

The second series of tests evaluated concrete in the same manner and no reactions were observed.

The third series of tests was performed on old asphalt to establish a threshold energy level. The material was found to be sensitive at impact energies even as low as 1 kg-m. After completing the third series of tests, another series of tests was performed on the old asphalt and photographed to show intensity of some of the more typical reactions. Results of the first three series of tests are shown in Table 1.

The final series of laboratory tests, using the same ABMA tester, evaluated old asphalt under special conditions. The major difference between these and the previous tests were sample size and amount of LO_2 used. The first sample, a 5-cm by 5-cm by 2.5-cm piece of asphalt immersed in approximately 0.15 liter of LO_2 , yielded

Table 1. Results of MSFC-SPEC-106-B LO₂ Paving Materials Impact Tests

Energy Level - 10 kg-m

| Materials Description | No. of Drops | No. of Reactions | Type of Reactions** |
|---|--------------|------------------|---|
| New Asphalt: 0.64 cm thick | 20 | 18 | 7 faint 2 violent 3 slight 6 appreciable |
| New Asphalt: several 0.19 cm specimens | 20 | 19 | 8 faint 11 slight |
| Old Asphalt: 0.64 cm thick | 20 | 20 | 6 appreciable 14 violent |
| Old Asphalt: several 0.19 cm specimens | 20 | 20 | 5 faint 15 slight |
| Concrete: 0.64 cm thick | 20 | 0 | --- |
| Concrete: several 0.19 cm specimens | 20 | 0 | --- |
| Old Asphalt: 0.64 cm thick | 3* | 3 | 1 slight 1 appreciable 1 violent |

* 1 kg-m energy level

** Faint - Barely visible light flash.
Slight - Light flash easily seen.
Appreciable - Intense light flash sometimes accompanied by audible report.
Violent - Very intense light flash accompanied by loud audible report.

a violent reaction. The second sample, essentially a cube 7.5 cm on a side, failed to react on the first drop; however, the test specimen broke into several pieces. Without adding additional LO_2 or changing the sample, a second drop produced a very violent reaction. The last sample, which was approximately 12 cm by 12 cm by 7.5 cm (immersed in approximately 0.5 liter of LO_2) again failed to react on the first drop; but, like the second specimen, it broke into several pieces. Again without changing the sample, the plummet was dropped a second time. This time another violent reaction occurred which threw a 5.89-kg stainless steel backup plate a couple of meters into an aluminum door, and also damaged the plummet spider and four mounting studs (see Figure 1). The test sample was blown into a large number of tiny pieces.

Field Experiments

First Trial, Impact. - A test stand, shown in Figure 2, was fabricated to support four plummets, each held by a pin with a lanyard to permit remote individual release. The plummets weighed 9.07 kg and were 7.5 cm in diameter. Tips, 1.27 cm in diameter and approximately 3.8 cm long, were screwed into the bottom of each plummet. Each plummet was provided with a tube extending to within approximately 15 cm of the surface to be impacted. This prevented a plummet from falling over after being dropped and interfering with the impact of subsequent plummets. A rod screwed into the side of each plummet and extending through a vertical slot in each tube provided a handle by which the plummet could be raised to the top of its tube to be secured by a release pin. A slab of used asphalt pavement 2 meters square and approximately 5 cm thick was installed at the test site and an asphalt curb 7.5 cm high was built around its edge. The test stand was assembled over the slab with its feet level with the asphalt surface. A ring of flex line, perforated on the bottom, was coupled to the LO_2 delivery line and positioned over the middle of the slab. The slab was sponged dry to remove rainwater, and then a trial flow of LN_2 was performed. Three days later a 400 frame per second movie camera was installed, rainwater was again sponged from the slab, and 12 empty 0.5 liter aluminum beer cans were placed as shown in Figure 3 as blast



Figure 1. LOX Impact Test Cell after LOX/Asphalt Reaction.

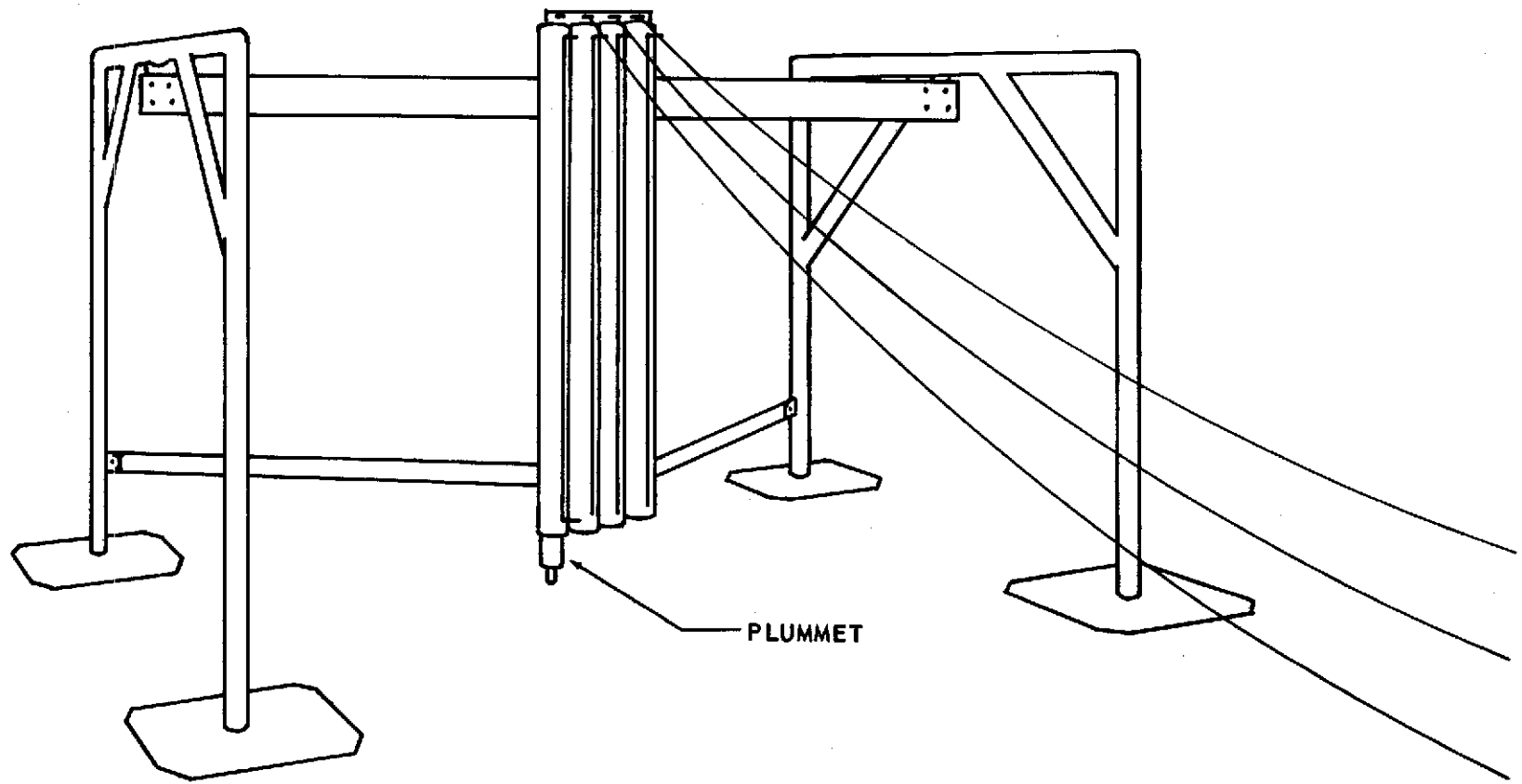


Figure 2. Impact Test Stand.

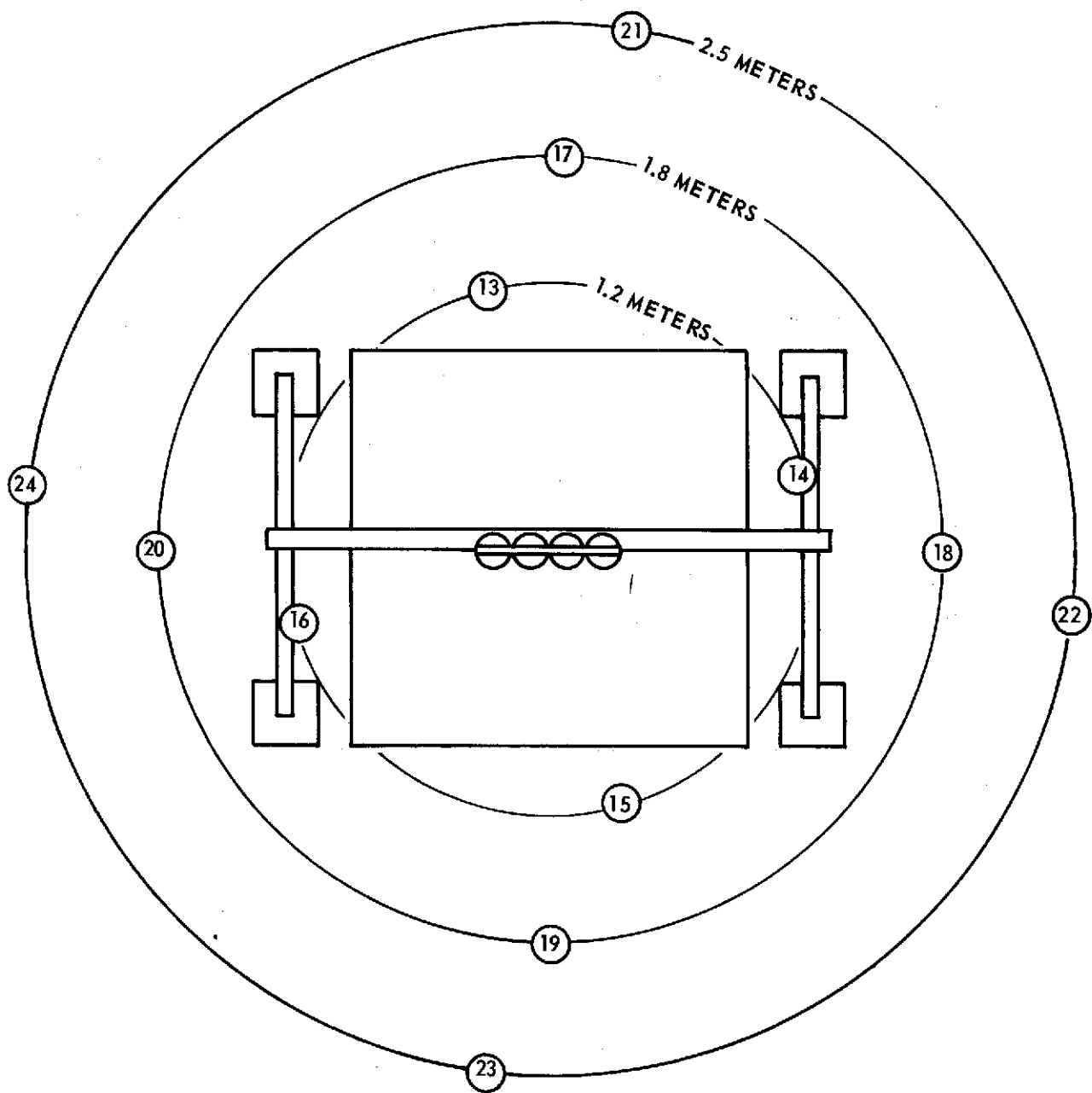


Figure.3. Blast Sensor Location, Impact.

sensors. The slab was then filled with LO_2 , which was allowed to flow for 10 minutes, and the four plummets were then dropped in succession with no detectable reaction.

Second Trial, Impact. - The tips were then removed from the plummets, a notch was cut in the curb to reduce the LO_2 depth to 1.77 cm, and the test was repeated with a 7.5-cm diameter impact area. No reaction was detected. It was found that the tips had penetrated the slab during the four impacts of the first trial.

Third Trial, Detonation. - The holes and the notch were repaired, the test fixture was removed, and rainwater was sponged from the slab. A No. 8 blasting cap with 15 cm of 21 gm per meter detonating cord was positioned on the slab. LO_2 was allowed to flow for 10 minutes; then the cap was detonated. Some smoke and flame occurred, but the reaction was confined to approximately a 2.5-cm depth of asphalt over an area of approximately 0.09 m^2 . Some beer cans, which were positioned as shown in Figure 4, had been overturned, but by the wind rather than the detonation. One can, No. 4, had been burned, and another, No. 3, had been struck by a small object which scratched the paint, but did not deform the can.

Fourth Trial, Impact. - A concrete slab, 1 meter square and 15 cm thick, was then placed on the test site with its top surface at grade level. A slab of new asphalt 2 meters square and a minimum of 10 cm thick was laid over the concrete, and a 7.5-cm high asphalt curb was built around its edge. The following morning, after sponging rainwater from the slab, LO_2 was allowed to flow for 10 minutes, and four plummets with tips installed were dropped in succession without reaction. The tips had penetrated the asphalt approximately 1.8 cm.

Fifth Trial, Impact. - A 15-cm long tip was then installed on the first plummet, a 15-cm tip with the end ground to 0.6 cm in diameter was installed on the second plummet, and the four plummets were raised so that the tips would strike in the same locations as before. LO_2 was then allowed to flow for 4 minutes, and was terminated because of a leak in a delivery valve. The slab was full and overflowing, however, and the four plummets were dropped in succession, but no reaction occurred. It was estimated that the tips had penetrated the asphalt an additional 0.6 cm.

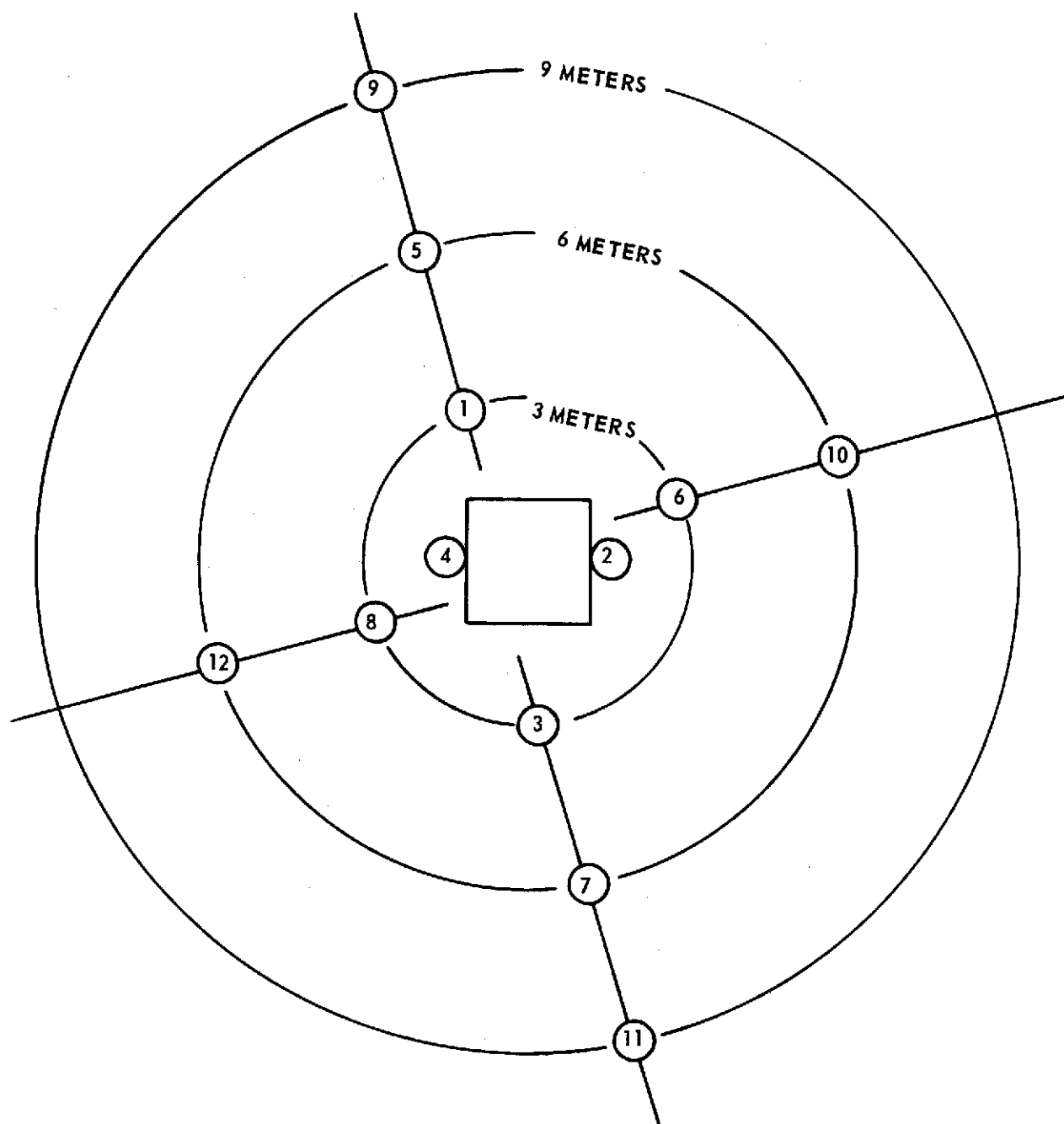


Figure 4. Blast Sensor Location, Blasting Cap.

Sixth Trial, Impact. - The test stand was then removed, and a trench about 50 cm long, 10 cm wide, and 1.2 cm deep was chiseled in the asphalt. In the position where the second plummet would strike, an additional cavity was excavated to accommodate a 2.5-cm thick aluminum block, 9 cm wide and 10 cm long. The block was firmly seated with its top surface slightly below the level of the slab surface. A mixture of broken old and new asphalt pavement, ranging from small pea size to large nut size, was piled in the trench and tamped by foot. The pile was from 1 to 2 cm above the slab surface. The test stand was then repositioned. No change was made in the plummet tips, but a striker pin, consisting of a 1.2-cm threaded rod about 22 cm long, with a 7.5-cm teflon disc at the top was placed on the asphalt under the third plummet, with the disc inside the tube to support it. Figure 5 shows the impact points prepared for this trial. Beer cans were positioned as shown in Figure 2. LO_2 was allowed to flow for 10 minutes, the camera switch was activated, and the first plummet was released, with no reaction. The second plummet was then released, and a detonation occurred. The test stand was destroyed, and it is estimated that pieces of it rose 30 meters in the air. When the test site was inspected, it appeared that a reaction had occurred over the entire slab surface, but only a small proportion of its material has been consumed to an estimated depth of 2.5 cm. The reaction appeared to have initiated at two points, above and below the aluminum block. The plummet tip impression in the aluminum block was several times deeper than one made by simply dropping the plummet from the same height. A cavity was found in the asphalt under the position occupied by the aluminum block. It was found that the camera had not been actuated by the switch, and no film of the reaction is available. Still photographs were made of the debris in situ. Figures 6 and 7 show the impact site. In Figure 7, the outline of the asphalt slab can be seen. Fragments have been assigned identification numbers 1 through 33. Figure 8 shows fragments 16, 17, and 18 at a distance of approximately 30 meters from the impact point. Figure 9 shows fragment 15, approximately 9 meters from the impact point. Figure 10 shows a plummet, fragment 28, approximately 12 meters from the impact point. Figure 11 shows a leg, fragment 22, approximately 47 meters from the impact point. Although the holding pond was contaminated, two objects were retrieved from it: the first plummet, and the



Figure 5. Points of Impact Prepared for Sixth Trial.



Figure 6. General View, Impact Site after Detonation.

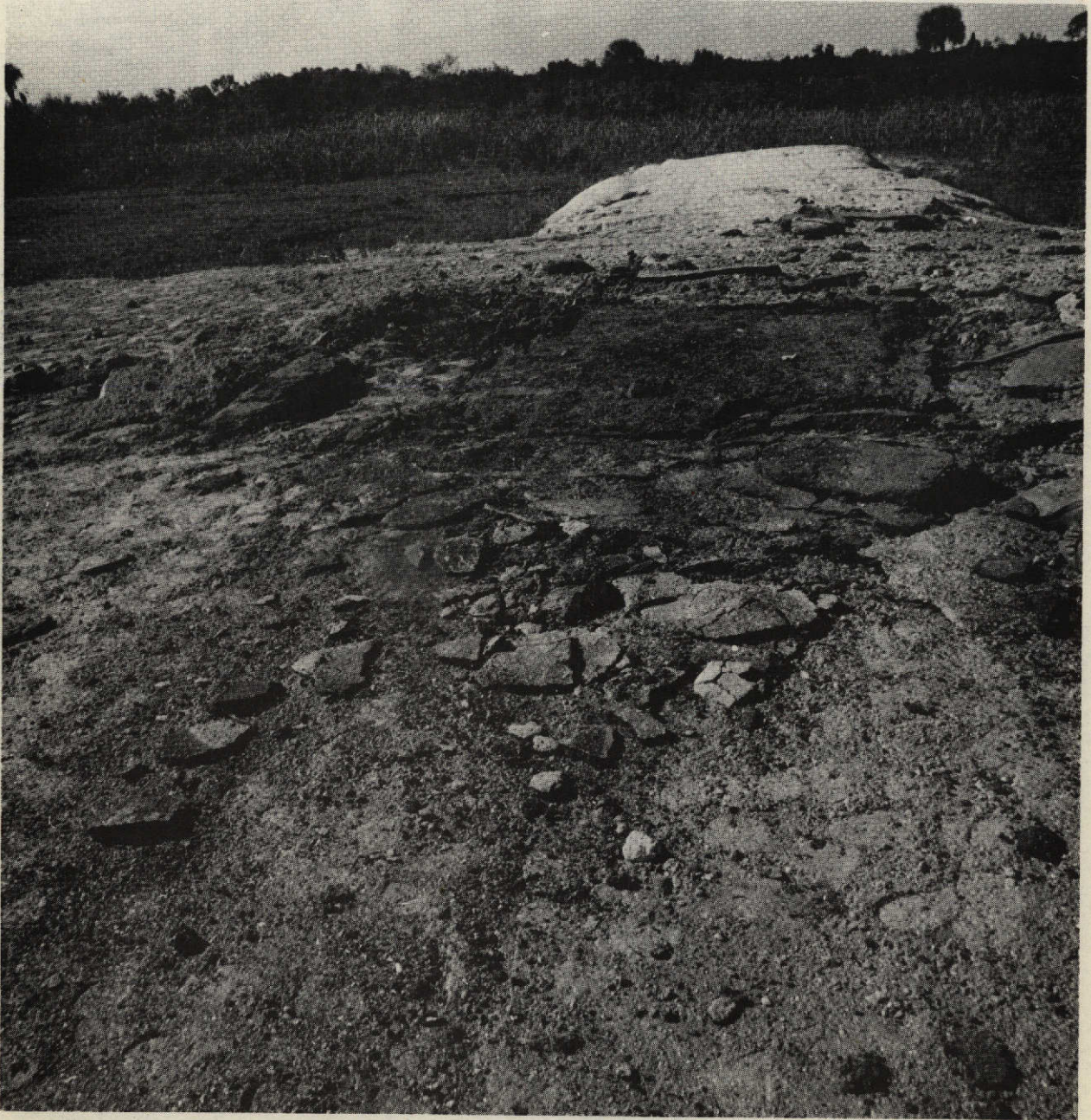


Figure 7. Impact Site, View from East.



Figure 8. View to North. Fragments 16,
17, and 18.

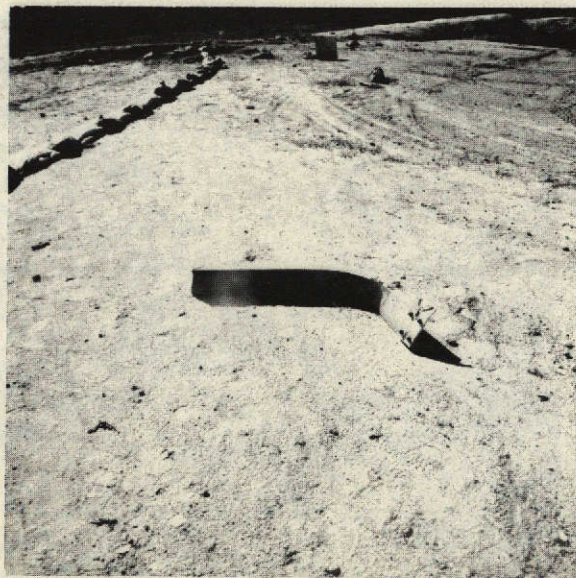


Figure 9. View from Northeast.
Fragment 15.

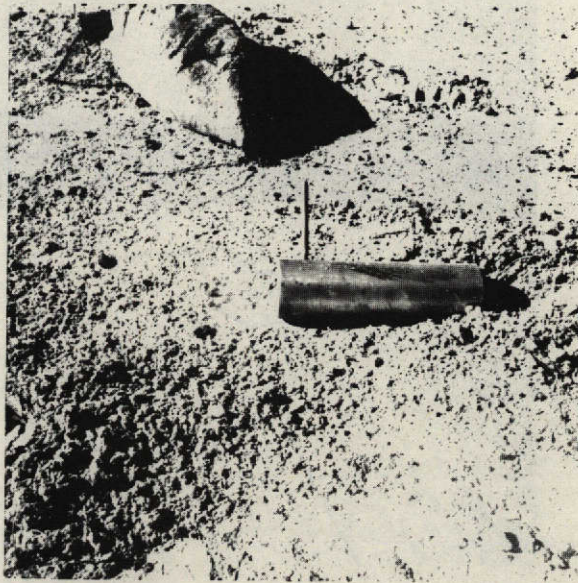


Figure 10. Plummet, Fragment 28.



Figure 11. Leg, Fragment 22.

aluminum block which had been placed under the second plummet. The block (a, Figure 12) was approximately 18 meters at 92° from the impact point. The plummet was approximately 33 meters at 94° from the impact point. The fragments were then located, collected, weighed, photographed, and plotted on a map. Figures 13 through 19 are photographs made at that time showing representative fragments. Figure 20 is a map of the area, showing the position of fragments after the detonation. Table 2 shows the weights, distances, and azimuths for the fragments. In the last trial, three conditions were different from those of the previous trials: first, the asphalt had dried out during a dry, warm week-end before this trial, while all other trials had been made after wet slabs were sponged dry; second, asphalt at the point of impact was broken, presenting a larger surface area; and third, an aluminum block was placed beneath the broken asphalt at the point of impact.



Figure 12. Aluminum Block.



Figure 13. Guide Tubes, Fragment 4.



Figure 14. Flex Hose, Fragment 19.



Figure 15. Leg, Fragment 21.

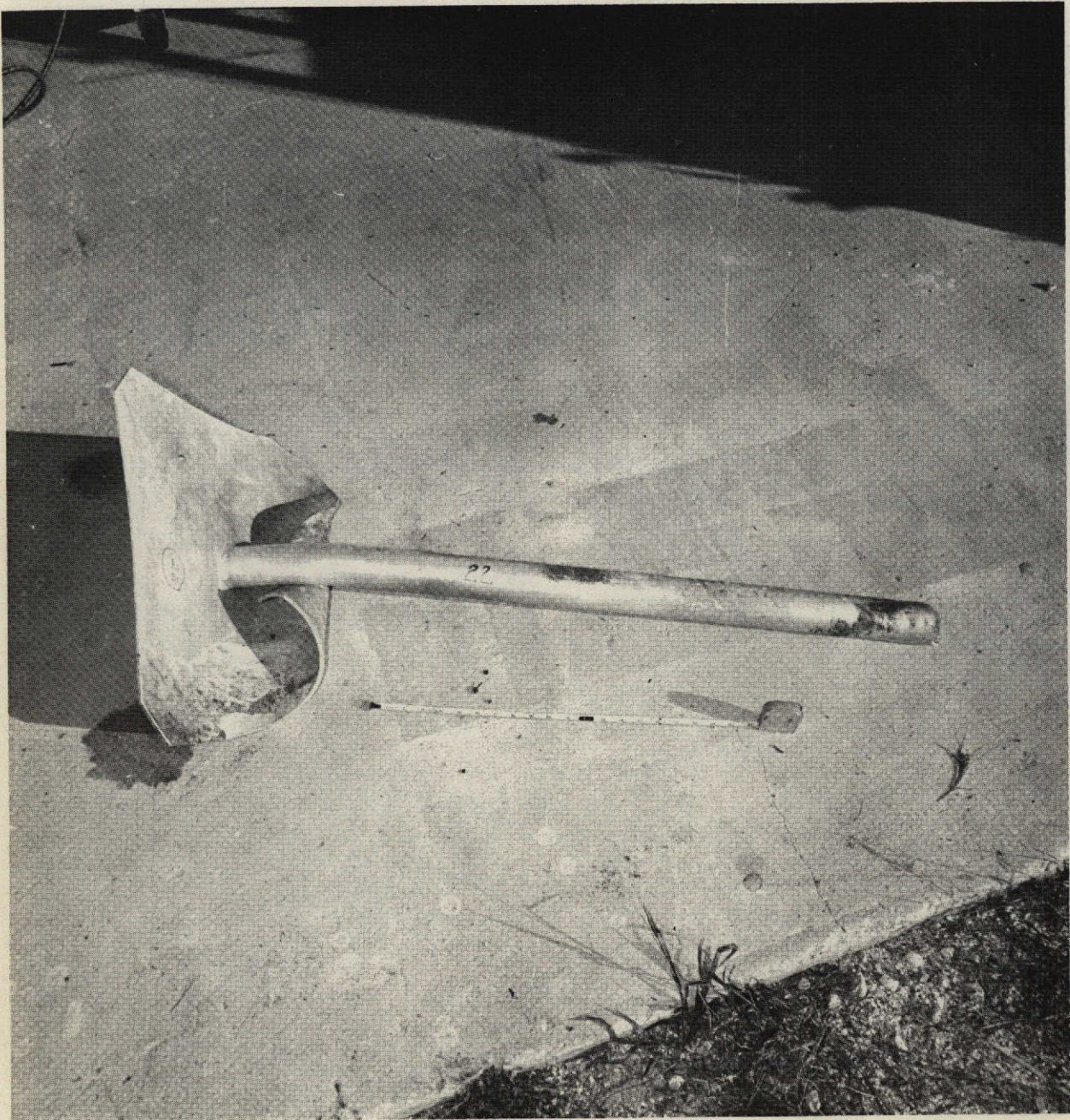


Figure 16. Leg, Fragment 22.



Figure 17. Channel, Fragment 23.

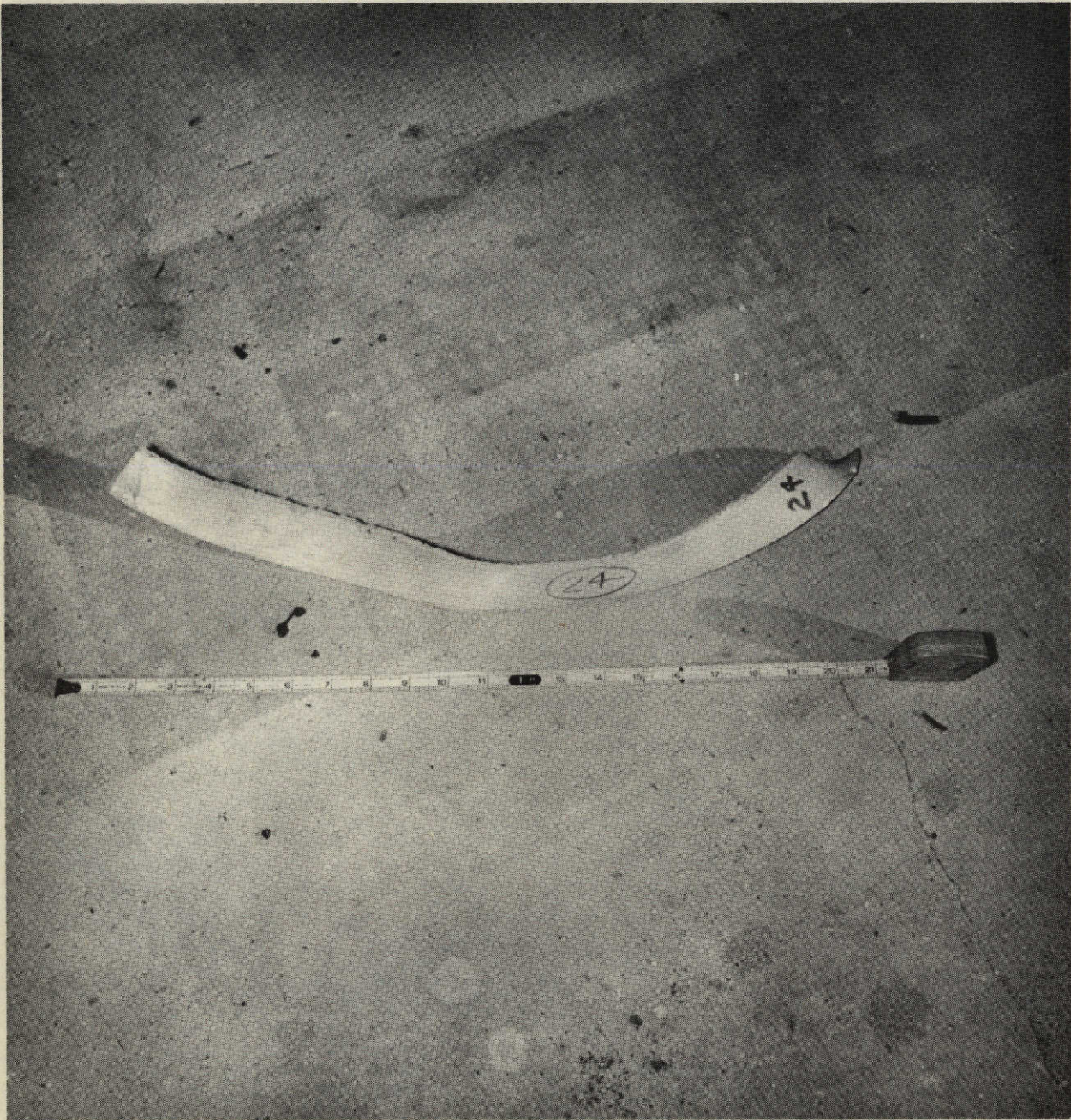


Figure 18. Aluminum Fragment 24.



Figure 19. Asphalt Fragments.

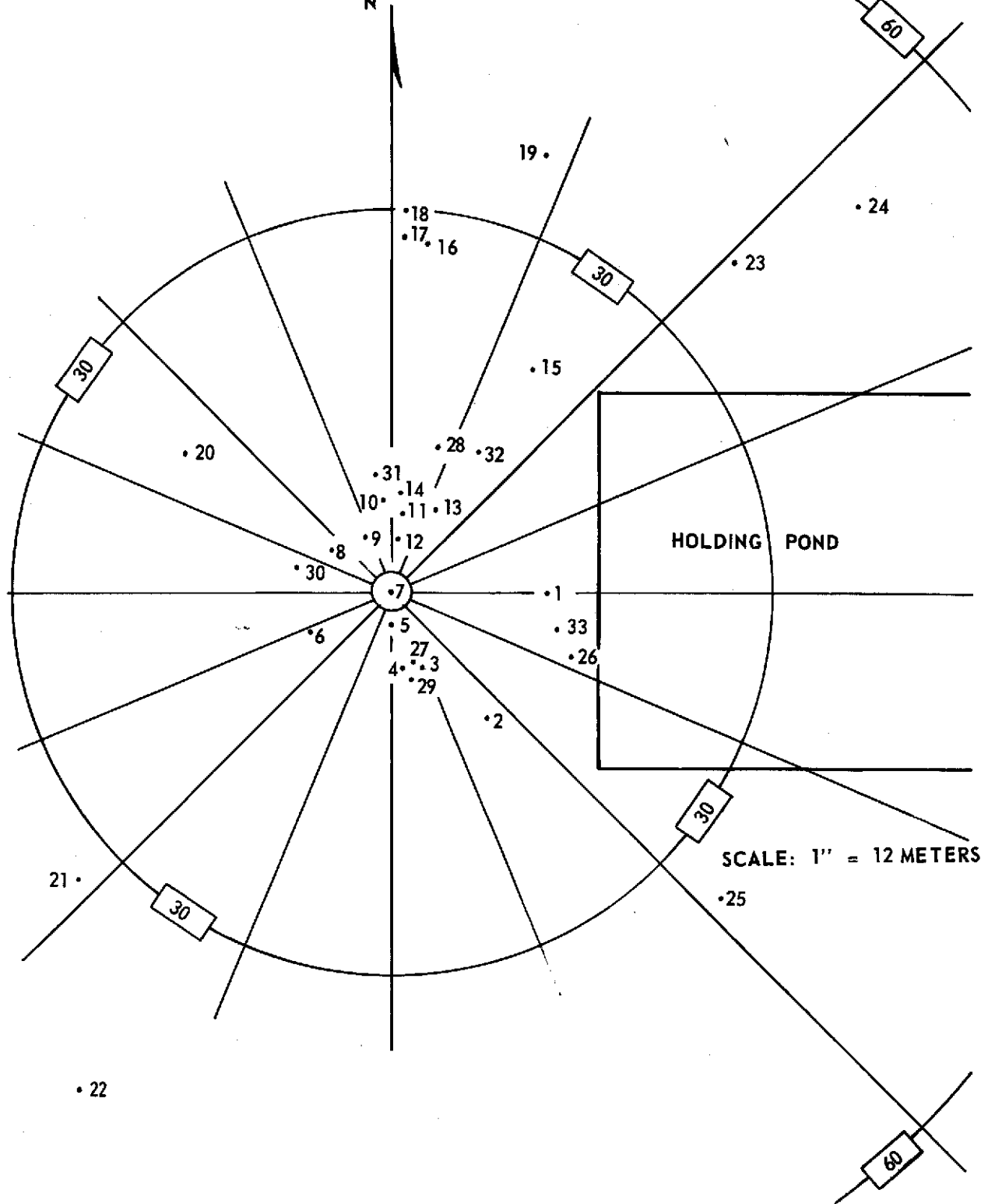


Figure 20. Map of Fragment Location

Table 2. LOX/Asphalt Test Debris Location

| Item No. | Debris Description | Distance From Impact Point (Meters) | Azimuth (Degrees) | Weight (Kilograms) |
|----------|--------------------------|---|----------------------|-----------------------|
| 1. | Blast Sensor Fragment | 12.6 | 90.0 | --- |
| 2. | Guide Tube | 12.7 | 143.0 | 6.03 |
| 3. | Blast Sensors | 6.7 | 157.5 | --- |
| 4. | 1 plummet, 2 guide tubes | 6.1 | 172.5 | 21.93 |
| 5. | Piece of Blast Sensor | 2.6 | 180.0 | --- |
| 6. | Piece of Blast Sensor | 7.3 | 244.0 | --- |
| 7. | Piece of Blast Sensor | 0 | --- | --- |
| 8. | Blast Sensor | 5.8 | 304.0 | --- |
| 9. | Blast Sensor | 4.8 | 332.5 | --- |
| 10. | Blast Sensor | 7.4 | 354.5 | --- |
| 11. | Blast Sensor | 6.4 | 9.0 | --- |
| 12. | Blast Sensor | 4.2 | 9.0 | --- |
| 13. | Blast Sensor | 7.6 | 27.5 | --- |
| 14. | Leg | 8.0 | 5.5 | 6.35 |
| 15. | Channel | 19.7 | 32.5 | 4.76 |
| 16. | End Frame | 28.0 | 5.5 | 8.16 |
| 17. | Leg | 28.5 | 2.0 | 6.29 |
| 18. | Guide Tube | 30.6 | 2.0 | 5.89 |
| 19. | Flex Hose | 37.3 | 19.5 | 6.8 |
| 20. | Blast Sensor | 19.7 | 304.0 | --- |
| 21. | Leg | 35.6 | 228.0 | 4.42 |
| 22. | Leg | 47.0 | 212.5 | 6.69 |
| 23. | Channel | 38.3 | 46.0 | 4.76 |
| 24. | Part of Brace | 48.5 | 21.0 | 3.17 |

Table 2. LOX/Asphalt Test Debris Location (Continued)

| Item No. | Debris Description | Distance From Impact Point (Meters) | Azimuth (Degrees) | Weight (Kilograms) |
|----------|--------------------|---|----------------------|-----------------------|
| 25. | Aluminum Fragment | 36.1 | 132.5 | 0.0028 |
| 26. | Aluminum Fragment | 15.5 | 109.0 | - - - |
| 27. | Plummet | 5.8 | 164.0 | 9.07 |
| 28. | Plummet | 12.1 | 18.0 | 9.07 |
| 29. | Asphalt Fragment | 7.1 | 166.5 | 0.54 |
| 30. | Asphalt Fragment | 7.9 | 284.0 | 0.023 |
| 31. | Asphalt Fragment | 9.5 | 353.0 | 0.034 |
| 32. | Asphalt Fragment | 13.0 | 32.0 | 0.028 |
| 33. | Asphalt Fragment | 13.9 | 102.5 | 0.018 |

APPENDIX A
SURVEY OF HAZARDS OF HANDLING LIQUID OXYGEN

NOTE

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Survey of Hazards of Handling Liquid Oxygen

With the increased industrial use of liquid oxygen, the importance of knowing about its compatibility with other materials is very much accented

ON THE International Temperature Scale of 1948 (14), the boiling point of oxygen is, by definition, -182.970°C ., at a pressure of 1 standard atm. At a pressure of 1 atm., liquid oxygen has a density of 1.14 grams per cm^3 and a heat capacity of 0.394 cal. per gram $^{\circ}\text{C}$. at a temperature just below the boiling point and a heat of vaporization of 50.9 cal. per gram (4). Oxygen has a critical temperature of -118.8°C ., critical pressure of 49.7 atm., and a critical density of 0.430 grams per cm^3 (8).

On passing from the liquid state at the boiling point to the gaseous state at 20°C . (both at a pressure of 760 mm. of mercury), oxygen expands to about 858 times the initial volume. If the material were confined to the initial volume during this increase in temperature, the pressure would increase to about 2440 atm. (about 36,000 p.s.i.), as calculated by the method of Hirschfelder and coworkers (6) on the basis of the critical constants given above. Consequently, the rupture of liquid oxygen containers due to pressure is

likely if proper venting is not provided.

The properties of most materials are altered considerably when they are cooled from room temperature to the temperature of liquid oxygen (1, 5, 10). This fact must be borne in mind in designing equipment for storage and handling of liquid oxygen. With few exceptions, ferrous alloys are too brittle for use at these temperatures but the following metals are reported to be usable at the temperature of liquid oxygen and are listed in order of increasing brittleness: pure nickel, monel, inconel, copper, aluminum, 18-8 low carbon stainless steel, and annealed brass.

The differences in thermal coefficients of expansion of materials may give trouble where close dimensional tolerances must be maintained.

Contact of the flesh with materials at the temperature of liquid oxygen for more than a few seconds can cause tissue damage similar to that produced by severe burns. Protective clothing made of asbestos or degreased chrome leather lined with relatively impermeable materials

such as polyvinyl chloride, polyethylene, or neoprene has been recommended (10).

Violent boiling and splashing usually occur if liquid oxygen is poured into a container at or above room temperature or if any warm object is placed in contact with the liquid.

Liquid Oxygen with Other Materials

The oxygen concentration, in weight per unit of volume, of 98% pure liquid oxygen is about 4000 times that in dry air at 20°C . and 760 mm. of mercury, therefore, oxidation reactions, once initiated, proceed at very high rates in the presence of the liquid. Though it might seem that such a cold liquid would extinguish a burning match, the actual effect of such a combination is deflagration of nearly explosive violence (7). Finely divided charcoal, saturated with liquid oxygen, is an explosive similar in many respects to 40% nitroglycerine dynamite and is used as an industrial explosive (3, 11, 15).

Other materials that have been

used in this way are wood pulp, cotton, lampblack, carbon black, various chars, hydrocarbons, metal powders, sulfur, and coal dust (15). Mixtures of any of these materials and liquid oxygen detonate so readily that it seems likely that an intimate mixture of liquid oxygen and almost any combustible material might detonate under certain conditions. The following incident illustrates this point.

A leak was reported to have developed in a pipe joint in a liquid oxygen line and the liquid flowed onto an asphalt-paved surface directly below. When a workman attempting to repair the leak struck the joint, the impact was transmitted by the joint to the pavement below and the pavement detonated.

Among the materials considered particularly hazardous in the presence of liquid oxygen are sulfur, hydrocarbons, alcohols, ethers, fuels of all kinds, oils, greases, waxes, tars, asphalt, starches, sugars, soaps, powdered metals, wood, cork, paper, textiles, rope, paints, and some plastics (7, 3, 5, 7, 10-13, 15). As liquid oxygen is denser than water and most liquid petroleum products, it will sink in such materials and boil violently, producing an intimate mixture. Porous materials may retain a large concentration of gaseous oxygen long after the liquid has vaporized. The hazard represented by a small sample of a given material when soaked in liquid oxygen does not appear to differ appreciably between samples soaked for 24 hours and those immersed for 2 or 3 minutes.

Thermal insulating materials for use around oxygen containers must be chosen with due regard for the hazard which would result from a leak. Inorganic materials such as glass wool or magnesium carbonate may be used if they contain no flammable additives. Ordinarily, to avoid the flammability hazard of paint, pipe lines carrying liquid oxygen are not painted.

Gaseous Oxygen

In the gaseous state, at 0° C. and 760 mm. of mercury, oxygen has a density of 1.429 grams per liter. Oxygen constitutes about 21% by volume or about 23% by weight of the earth's normal atmosphere at

sea level. Besides the precautions necessary to prevent the rupture of containers due to pressure, it is necessary to provide sufficient ventilation in confined spaces to prevent excessive concentration of gaseous oxygen. In general, combustible materials burn violently in an atmosphere of oxygen. Materials, including metals, initially glowing or smoldering in air, burst into flame or brilliant candescence when introduced into oxygen. Mixtures of flammable vapors or dusts with gaseous oxygen may be explosive (15).

Although the human body can tolerate rather wide variations in the oxygen concentration in the atmosphere, prolonged exposure to an atmosphere containing 80% or more of oxygen can induce a pneumonia (9).

Ignition

The prevention of ignition is a matter of greatest importance wherever liquid oxygen is handled.

Friction in itself may be regarded as a possible source of ignition where oxygen is in contact with combustibles (15). A detonation was reported to have occurred when a man walked across a gravelled surface on which liquid oxygen had been spilled. Ignition was attributed to friction between gravel and the asphalt beneath.

A large number of materials may be placed in liquid oxygen for a few minutes and be detonated by impact.

On the basis of two experiments with a vegetable base fiberboard in an adiabatic furnace at the National Bureau of Standards, the rate of self-heating is not greatly affected by increased oxygen concentration in the atmosphere at temperatures below 200° C., but above 200° C. the rate of self-heating was considerably higher in the enriched atmosphere than it is in air. Materials containing unsaturated hydrocarbons should be considered particularly hazardous in this respect. Heaters and steam lines, which might not otherwise be considered hazardous ignition sources, might become so in the presence of an oxygen-rich atmosphere.

The lower limit of flammability of combustible gases generally occurs at about the same concentration in oxygen as in air (2).

Tests have shown that the liquid-oxygen explosives in use in industry were rather insensitive to ordinary electrostatic discharges and that the discharge energy required to constitute a hazard was considerably greater than would ordinarily be encountered—except where lightning or electric power line sparking is involved (15).

All personnel required to handle liquid oxygen should be trained by someone experienced in this field and be closely supervised until safe practices are established.

Literature Cited

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